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(54) PREPARATION OF N-PHOSPHONOMETHYL GLYCINE

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(57) Claim

1. Process for the preparation of N-phosphono-
ethyl-glycine by oxydating N-phosphonoethyl isino
dicetic acid with oxygen or a gas containing oxygen in
under heating or stirring
(conventional) or otherwise at a temperature of 20°C
the presence of a catalyst which comprises oxydating

N-phosphonoethyl isino dicetic acid in an aqueous

suspension.

COMPLETE SPECIFICATION

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Complete Specification for the invention entitled

PROCESS FOR THE PREPARATION OF N-PHOSPHONOMETHYL GLYCINE

The following statement is a full description of this invention, including the best method of performing it known to us

PROCESS FOR THE PREPARATION OF N-PHOSPHONOMETHYL GLYCINE

The present invention relates to an improvement in the process for the preparation of N-phosphonomethyl glycine by oxydation of N-phosphonomethyl imino dicetic acid with oxygen or a gas containing oxygen in the presence of a catalyst.

N-phosphonomethyl glycine has been known and widely used for almost a decade for its herbicidal activity. N-phosphonomethyl glycine (Glyphosate) is suitable for the control of various ~~monocotyledonous and undesired~~ 10 dicotyledonous annual and perennial plants in case of post-emergent treatment. A particular advantage of the compound is that it does not possess any persistent activity and thus it can be successfully employed in crop rotations (Proc. N. Cent. Weed Control Conf. 26, 15 64 /1971/).

N-phosphonomethyl-glycine is most often prepared by oxydation of N-phosphonomethyl iminodiacetic acid. One known process comprises oxydeting the starting material by hydrogen peroxide (Dutch Laid Open Patent 20 Publication No. 73 07 449). According to another method the carboxylic acid group of the starting material is split off by acid catalysed hydrolysis (Hungarian

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Patent Specification No. 165 965). Electrolytic oxydation is disclosed in German Federal Republic Patent Specification No. 2 363 634 US Patent Specification No. 3 859 183, and British Patent Specification No. 1 452 644. In reference No. 1 N-phosphonomethyl imino dicetic acid is subjected to anodic oxydation in acidic medium by using graphite electrodes, whereas the last two references relate to oxydation carried out on the tetraester group of N-phosphonomethyl imino dicetic acid and the aimed end product is formed by hydrolysing the obtained N-phosphonomethyl glycine triester.

Oxydation of N-phosphonomethyl imino dicetic acid may also be carried out with oxygen or oxygen-containing gas in the presence of a catalyst (US Patent Specification No. 3 959 388, German Federal Republic Patent Specification No. 2 519 388 and Belgian Patent Specification No. 661 995). The advantage of the catalytic oxydation over the known methods mentioned above is that it does not require expensive chemicals or electrolysing equipments. Severe drawbacks of this method, however, comes from the fact that N-phosphonomethyl imino dicetic acid used as starting material is poorly soluble in water (saturation concentration of the compound at 25°C: 1 % by weight, at 55°C: 4 % by weight and even at 150°C i.e. even in excess when operations are conducted at a higher pressure than normal pressure, the solubility amounts only to 10 % by weight (see German Federal Republic Patent Specification No. 2 519 388).

As a consequence of the minimal solubility of N-phosphono-
ethyl imino dicetic acid aqueous solutions have to be
employed in a large amount reducing thereby the useful
capacity of the reactor and increasing thus the required
5 energy. A large amount of water has to be recovered from
the effluents requiring a further amount of energy. This
process is thus uneconomical considering both utilization
of capacity and energy balance.

In order to eliminate the disadvantages mentioned
10 above a method is disclosed in Belgian Patent Specifica-
tion No. 851 995, according to which the salts of
N-phosphonomethyl-imino dicetic acid are used as
starting material. Depending upon the character of the
cation being present, the salts of N-phosphonomethyl imino
15 dicetic acid form a 5-30 % saturated solution with water
of a temperature of 100 °C. From the point of view of
energy-saving only those salts may be used in large
scale practice, the solubility of which is close to the
upper limit of the saturated concentration. Thus for
20 example isopropyl amino salt of N-phosphonomethyl imino
dicetic acid may be employed. Data disclosed in Belgian
Patent Specification No. 851 995 show that during
oxidation of the compound a considerable amount of by-
products is formed (such as N-ethyl-N-phosphonomethyl
25 glycine and ethylethylene ethyl phosphonic acid), which
reduces the yield of the end-product and may be recovered
from the end-product only with difficulties. Though the
formation of by-products may be reduced if conventionally

used chlorous catalysts are replaced by platinum catalyst (in this case the rate of the main reaction is selectively increased) side reactions however can never be eliminated completely. A further disadvantage is the low yield of the reaction: isopropylamine salt of N-phosphenoethyl glycine is obtained even in the most favourable case in the form of about 20 % aqueous solution, thus still a large amount of water has to be removed from the solution (about 50 %) if the product is formulated in the commercially available form of a 55 % aqueous solution. This process is however somewhat more economical than the previous process, but neither the purity of the product nor the energy balance of the process are satisfactory.

15 According to the invention the disadvantages of the considered known processes are eliminated by preparing pure N-phosphenoethyl glycine by an economic, energy-saving and capacity-increasing process.

16 We have now found that catalytic oxidation of N-phosphenoethyl isino dicarboxylic acid may be carried out in suspension converting thus N-phosphenoethyl isino dicarboxylic acid completely to N-phosphenoethyl glycine with a high specific conversion (related to the total and measured liquid volumes).

20 The process according to the invention has not claimed in the light of the disclosure of German Federal Republic Patent Specification No. 2510 303. On the contrary in the cited reference a process is disclosed

comprising the oxydation of N-phosphonoethyl isino dicetil acid carried out in aqueous solutions and not even the use of supersaturated solutions is suggested because "the precipitation of the starting material can be expected whereby the reaction is slowing down and the separation and purification of the product becomes more difficult."

Similar conclusions could be drawn when considering the reaction mechanics of suspensions. As the reaction may take place only on the boundary surfaces, it can be expected that the reaction - if it takes place at all - will be extremely slow from the beginning, the rate of reaction will gradually decrease with accumulating end-product and when achieving a given concentration the reaction substantially comes to an end as the molecules of the end-product formed on the boundary surface can diffuse only very slowly into the inner part of the liquid layer. Thus even in the most favourable cases only very slow reactions will be expected in suspensions, even 25% conversion is not achieved. We have now surprisingly found that the amount of the starting material converted within one time unit (expressed in g/g) in a suspension is about twice as much as the amount obtained in the reaction conducted in liquid layer and at the same time the starting material can be completely converted to the end-product. It has to be said that one of the conventionally used methods is used in order to accelerate the reaction in suspensions

(such as pregrinding in a colloid mill, treatment with wetting agents etc.).

The invention relates to an improvement in the process for the preparation of N-phosphonosethyl glycine

5 by oxydation N-phosphonosethyl imino diacetic acid with oxygen or oxygen-containing gas in the presence of a catalyst. The process is characterized by conducting the oxydation of N-phosphonosethyl imino diacetic acid in an aqueous suspension.

10 The content of N-phosphonosethyl-imino diacetic acid of the aqueous suspension may vary within a relatively wide range. The lower limit is given by the solubility of N-phosphonosethyl imino diacetic acid at a given temperature, while the upper limit depends on the 15 miscibility of the reaction mixture. If the reaction is carried out at 100 °C, then 5 % suspensions may be used as a lower limit but obviously suspensions containing 30-40-50 % of solid may preferably be used.

20 Oxydation is carried out with oxygen or a gas mixture containing oxygen, such as air. If as oxydating agent pure oxygen is employed, the rate of reaction is higher than the rate of oxydation conducted with air, but considering the needed equipment, energy and labour that pure oxygen is prepared, it is more economic to use air as oxydating agent.

25 The reaction temperature may vary within relatively wide limits. The reaction is carried out at a temperature ranging from room temperature to 200 °C, preferably from

50 to 150 °C, nor preferably from 70 to 120 °C.

The reaction may be conducted at normal pressure but the reaction rate is rather low when working under normal pressure. The reaction is preferably carried out at 5 elevated pressure, such as 2-20 atm. It is particularly preferred if the reaction is conducted at 4-10 atm. Further improvement is not achieved, when increasing pressure above this value.

10 Oxydation is always conducted under shaking or stirring. The rate of shaking or stirring should be sufficient to give a homogeneous suspension, local inhomogeneities may slow down the reaction and thus the end products may contain impurities.

15 As catalysts known catalysts, such as powder forced or granular charcoal (e.g. German Federal Republic Patent Specification No. 2 519 388), noble metal catalysts on a carrier (e.g. platinum or palladium applied on active charcoal), noble metaloxyde catalysts (such as platinum oxyde) and so on may be employed.

20 Noble metal catalysts applied on active coal (preferably platinum and palladium catalyst) ensure a higher initial rate of reaction than the active coal catalysts, i.e. they act as rate increasing catalysts as disclosed in Belgian Patent Specification No. 861 996. Active charcoal may be separated by simple filtration and it may be fully recovered by washing with hot water and by drying at 100-120 °C. The separated catalyst may be suspended in hot water followed by a treatment with an

oxygen-containing gas, e.g. with air and followed by drying. The catalytic activity of the recov red cataly t has not decreased after 10 working cycles.

According to Belgian Patent Specification No.

5 ESL 995 active charcoal used as a catalyst of the oxydation carried out in a solution loses its activity after a few cycles and cannot be recovered anymore.

According to the invention, however no significant losses in the material were observed in the course of the recovery of the catalyst.

At least 5 mg. of catalyst are used per 1 g. starting N-phosphonomethyl imino dicetic acid. The upper limit of the amount of the catalyst is substantially given by economic viewpoints. The amount of the catalyst may 15 be e.g. 0.5-100 %, preferably 5-60 %, particularly 5-40 % of the amount of N-phosphonomethyl imino dicetic acid.

According to the process of the invention N-phosphonomethyl glycine is obtained in the form of a pure product shown by NMR spectroscopy. The obtained 20 aqueous solution may be concentrated, if desired, according to the demands of the user, or N-phosphonomethyl glycine may be separated in solid form as well. Solutions obtained according to the invention and containing N-phosphonomethyl glycine may after distilling off 25 furfuraldehyde, directly be employed for agrochemical purposes.

These further Examples serve merely as illustration and not for limitation.

Example 1

Comparative Example

The reaction is carried out in an acid-fast
200 ml. cylindrical steel tank equipped with a heating
5 jacket, thermometer, and an air-introducing and air-outlet
valve. To the reactor a solution of 4 g. of N-phosphono-
ethyl imino dicetic acid in 100 ml. of water of a
temperature of 100 °C is added and to the solution 0.4 g.
of Norit A catalyst is introduced. The reactor is
10 sealed, fixed on a shaker and to the reactor air is
introduced until a pressure of 6 atm. is achieved. The
reaction is carried out at 90-95 °C under steady stirring
of the reactor. The formaldehyde and carbon dioxide
formed during the reaction is blown out from the reactor
15 every 30 minutes. Under such conditions the reaction is
completed within 2.5 hours and thus 2.8 g. (100 %) of
pure N-phosphonoethyl glycine are obtained (purity
verified by NMR spectroscopy). Specific conversion is
calculated according to the following formula:

20
$$\text{specific conversion} = \frac{\text{weight of end product (g.)}}{\text{volume of liquid (liter)} \times \text{reaction time (hour)}}$$

Specific conversion: 11.2 g./l.hour

25

Example 2

One may proceed according to Example 1 but as
starting material 100 g. of water, 20 g. of N-phosphono-
ethyl imino dicetic acid and as catalyst 2 g. of Norit

A are used. After a reaction time of 6.5 hours 14 g. of N-phosphonomethyl glycine are obtained and thus the specific conversion amounts to 21.5 g./liters.hour. (1.9 times more than the value achieved according to 5 the comparative Example).

Example 3

One may proceed as disclosed in Example 1 but as starting material 100 g. of water, 40 g. of N-phosphonomethyl imino dicetic acid and as catalyst 4 g. 10 of Norit A catalyst are used. After a reaction time of 10 hours 28.6 g. of pure N-phosphonomethyl glycine are obtained (verified by NMR spectroscopy). Specific conversion: 28.6 g./liters.hour (2.5 times more than the value obtained in the comparative Example).

15

Example 4

One may proceed as disclosed in Example 1 but as starting material 100 g. of water, 30 g. of N-phosphonomethyl imino dicetic acid and as catalyst 3 g. of Norit A catalyst are employed. After a reaction time of 8.5 hours. 20 21.2 g. of pure N-phosphonomethyl glycine are obtained (verified by NMR spectroscopy). Specific conversion: 24.9 g./liters.hour (2.2 times more than the value achieved by the comparative Example).

Example 5

25 The reaction is carried out in a 2 liters acid-

fast and pressure resisting steel autoclave equipped with a heating jacket, thermometer, air introducing and air outlet valve and paddle stirrer. To the autoclave 300 g. of N-phosphonomethyl imino dicetic acid, 1000 ml. of water and 30 g. of Norit A are introduced. The autoclave is sealed, the reaction mixture is heated to 90-95 °C, and air is led to the autoclave under the liquid level until 6 atm pressure is achieved. The suspension is stirred at a rate of 400 rpm. After a reaction time of 8.5 hours 208 g. of pure N-phosphonomethyl glycine are obtained, the purity of which is checked by NMR spectroscopy. Achieved specific conversion: 24.4 g./liters.hour (2.2 times more than the value obtained by the comparative Example).

15 When the reaction is completed, the catalyst is immediately filtered off, the mixture is washed with hot water and dried at 110 °C. The thus recovered catalyst is used in further operations.

Example 6

20 One may proceed as disclosed in Example 5, but as starting material 1000 ml. of water, 200 g. of N-phosphonomethyl imino dicetic acid and as catalyst 20 g. of Norit A recovered as disclosed in Example 5 are used. After a reaction time of 6.5 hours, 146 g. of N-phosphonomethyl glycine, the purity of which is verified by NMR spectroscopy, are obtained. Achieved specific conversion: 22.4 g./liters.hour (twice the value obtained

in the comparative Example).

The catalyst is recovered as described in Example 5 and used in further operations.

Example 7

5 One may proceed as described in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphono-methyl imino diacetic acid and as catalyst 2 g. of Norit A catalyst-recovered again after the reaction disclosed in Example 6-a is used. After a reaction time of 6.5

10 hours 14.2 g. of pure N-phosphonomethyl-glycine are obtained, the purity of which is verified by NMR spectroscopy. Achieved specific conversion: 21.8 g./liters.hour (1.9 times more than the value achieved according to the comparative Example).

15 The catalyst is used in further five working cycles after recovery. The activity of the catalyst is not reduced.

Example 8

20 One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphono-methyl imino diacetic acid and as catalyst 5 % palladium/charcoal (Carbo C Extra) are employed. After a reaction time of 5 hours 14.4 g. of pure 4-phosphono-methyl glycine are obtained, the purity of which is

25 verified by NMR spectroscopy. Achieved specific conversion: 28.8 g./liters.hour (2.5 times more than the

value obtained in the comparative Example).

Example 9

One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphono-
5 methyl imino diacetic acid and as catalyst 2 g. of Carbo C Extra are employed. After 7 hours reaction time 14.3 g. of pure N-phosphonomethyl glycine are obtained the purity of which was checked by NMR spectroscopy. Achieved specific conversion: 20.8 g./liters.hours (1.85
10 times more than the value achieved by the comparative Example).

Example 10

One may proceed as disclosed in Example 1 but as starting material 100 ml. of water, 20 g. of N-phosphono-
15 methyl imino diacetic acid and as catalyst 2 g. of 5 % platinum/charcoal (Carbo C Extra) are used. After a reaction time of 4.5 hours 14.2 g. of pure N-phosphono-
20 methyl glycine are obtained the purity of which is checked by NMR spectroscopy. The achieved specific conversion: 31.5 g./liters.hours (2.8 times more than the value obtained by the comparative Example).

When comparing data of Examples 8 to 10, it can be observed that by using noble metals the reaction rate may be increased.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:
~~SECRET~~

1. Process for the preparation of N-phosphono-methyl-glycine by oxydizing N-phosphonomethyl imino diacetic acid with oxygen or a gas containing oxygen ^{under shaking or stirring} in (conventional) at a temperature of between room temperature and 200°C in the presence of a catalyst which comprises oxydizing N-phosphonomethyl imino diacetic acid in an aqueous suspension ^{therefore}.
2. A process as claimed in claim 1 comprising using a suspension containing 7-70 g. of N-phosphono-methyl imino diacetic acid related to 100 ml. water as starting material.
3. A process as claimed in claim 2 which comprises using a suspension containing 20 to 50 g. of N-phosphono-methyl imino diacetic acid related to 100 ml. of water as starting material.
4. A process as claimed in any of the claims 1 to 3 which comprises using air as a gas containing oxygen.
5. A process as claimed in any of the previous claims, which comprises conducting the reaction at elevated pressure.
6. A process as claimed in any of the previous claims which comprises using active charcoal as catalyst, separated after the reaction by filtration and recovered by washing with hot water, and drying at 100 to 120 °C.
7. A process as claimed in claim 6 which comprises washing the catalyst with hot water during the introduction of oxygen or a gas containing oxygen,



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preferably air ~~below~~ the liquid level.

DATED this 8th day of May 1980.

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